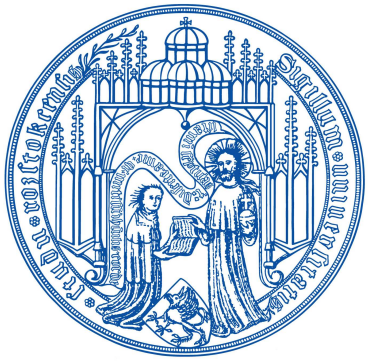
Spectroscopic Evidence for Clusters of like-charged Ions in Ionic Liquids

Cumulative Dissertation

to obtain
the academic degree
doctor rerum naturalium (Dr. rer.nat.)

of the
Faculty of Mathematics and Natural Science
at the University of Rostock



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Rostock, July 2017

urn:nbn:de:gbv:28-diss2018-0055-3

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Thesis submission: 26.07.2017
PhD defense: 17.10.2017

The present work was conducted during the period from October 2014 until July 2017 under the supervision of Prof. Dr. Ralf Ludwig in the Institute of Chemistry at the University of Rostock.

Acknowledgement

First and foremost, I would like to thank my supervisor Prof. Dr. Ralf Ludwig for giving me the opportunity to work in his research group and to work free and with own ideas on this very interesting topic. Your door was always open for scientific discussion and all questions one can imagine. Many thanks for your scientific support as well as your trust during my PhD time.

I extend my thanks to the DFG, to the University of Rostock, to the Woman Professorship Program and to the Graduate Academy of the University of Rostock for financial support.

A huge thanks goes to the whole research group Physical and Theoretical Chemistry, to all former and present colleagues, for a warm welcome and a pleasant working atmosphere. Especially I would like to thank Thomas Niemann, Peter Stange and Alexander Wulf for all the scientific discussions and suggestions as well as Anne-Marie Bonsa for measuring viscosities and having always a friendly ear. I also acknowledge Anika Wilhelms and Dagmar Klasen for the technical support. Additionally I would like to thank Dr. Dirk Michalik, Viktoria Lehde, Viviane Overbeck who contributed to this work with NMR measurements as well as Henning Schröder from the Institute of Mathematics who developped a new program for the deconvolution of IR spectra and accelerated my work extremely this way.

Finally and most importantly, I would like to thank my whole family, my parents, but especially my husband Mirko for your always constant encouragement, companionship, confidence and your love.

Abstract

Whereas ion pairing is one of the most fundamental atomic interactions in chemistry and biology, pairing between ions of like charge remains an elusive concept. This phenomenon was only reported for large scale structures, assemblies, stabilizing frameworks or aqueous solutions, wherein the like-charge attraction is mediated by solvent molecules. In this work the formation of cationic clusters in ionic liquids is described for the first time.
All investigated cations include hydroxyethyl functional groups, where the OH group is known for the formation of hydrogen bonds and the ethyl group realizes a large distance between the OH group and the center of positive charge. This way the like-charge repulsion is attenuated by cooperative hydrogen bonding as it is known for molecular solvents like alcohols. The cationic clusters (c-c) can grow from dimers, over linear trimers and tetramers up to cyclic tetramers. They are present together with cation-anion pairs (c-a) and favored at low temperatures. The equilibrium between both H-bond species (c-c and c-a) can be controlled by differently strong interacting anions.
Experimentally the cationic cluster formation is indicated by characteristic spectroscopic features. OH vibrational frequencies are redshifted compared to those observed for hydrogen bonds within the ion pairs. Even the average proton chemical shift of the OH group is shifted downfield if cationic clusters are present in the ionic liquid. These spectroscopic observables can be related to charge transfer and second order stabilization energies in the context of cooperative hydrogen bonding. Other properties, like larger intramolecular bond lengths and smaller intermolecular bond distances, also support this interpretation. Finally, a theoretical approach of stabilizing the cationic cluster network by either neutral molecules or negatively charged counterions has been done. This should be the starting point for future investigations in the gas phase.

Contents

List of Abbreviations

Cations:

$[Ch]^+$	(2-Hydroxyethyl)-trimethylammonium (Cholinium)
$[TMPA]^+$	N,N,N-trimethyl-N-propylammonium
$[HEMIm]^+$	1-(2-Hydroxyethyl)-3-methylimidazolium
$[PMIm]^+$	1-(2-Propyl)-3-methylimidazolium

Anions:

$[NTf_2]^-$	Bis(trifluoromethylsufonyl)imide
$[BF_4]^-$	Tetrafluoroborate
$[Tf]^-$	Trifluoromethylsufonate
$[Ms]^-$	Methylsulfonate
$[PF_6]^-$	Hexafluorophosphate

Other chemicals:

CCl_4	Carbontetrachloride
$CDCl_3$	Chloroform-d1
DM1B	3-3-dimethyl-1-butanol
DMSO	Dimethylsulfoxide
EtOH	Ethanol
TMS	Tetramethylsilane

Others:

AEHB	Anti-electrostatic hydrogen bond
AILs	Aprotic ionic liquids
B3LYP	Becke-3-parameter-Lee-Yang-Parr exchange correlation functional
c-a	Cation-anion
c-c	Cation-cation
CIP	Contact ion pair
EDA	Energy decomposition analysis
DFT	Density functional theory
FIR	Far infrared
IL	Ionic liquid
MIR	Mid infrared
NBO	Natural bond orbital
NOE	Nuclear Overhauser effect
NMR	Nuclear magnetic resonance
PILs	Protic ionic liquids
RTIL	Room temperature ionic liquid
SIP	Solvent separated ion pair

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1 Introduction

1.1 Ionic liquids

Ionic liquids (ILs) are a fascinating substance class that consists entirely of ions. [1] From literature they are known as salts with a melting point below 100°C [2], whereby this temperature is more or less arbitrary and is mainly used to differentiate them from common salts. In contrast to ionic solutions, ILs consist only of large asymmetric organic cations and small inorganic or organic anions, without any solvent molecules. [3]
Gabriel et al. synthesized the first ionic liquid ethanolammonium nitrate already in 1888. [4] Only some years later in 1914 the first room temperature ionic liquid (RTIL) ethylammonium nitrate with a melting point of 12°C was synthesized by Paul Walden. [5] During the following decades there was no large interest in this special substance class until inorganic chloroaluminates became more important in research in the mid-20th century. [6, 7] Since 1981 the cations of the chloroaluminates were changed from alkylpyridinium to dialkylimidazolium, leading to higher electrochemical stability and lower melting points. [8, 9] However, all of these chloroaluminates have in common that they are extremely hygroscopic. Thus, the synthesis of the first air and water stable imidazolium based ionic liquids in the early 90s was a huge advance in the direction of applications. [10] Based on these investigations a lot of different air and water stable ILs were synthesized in different working groups all over the world. [11–16] Today the most commonly used ILs are based on the ammonium-, imidazolium-, pyrrolidinium- or pyridinium cation and the methylsulfonate-, triflate-, tetrafluoroborate-, hexafluorophosphate or bis-(trifluoromethylsulfonyl)imide anion. Especially the fluorinated anions are prominent, because of the viscosity-lowering reduction of the van der Waals interactions.
Due to the huge variety of ion combinations the number of possible ionic liquids has been estimated to be in the trillions. [3] This impressive number allows a unique tailoring of physical and chemical properties, leading to the term "designer solvents". [17] Thus, the interest in ILs increased since the turn of the millennium and especially during the last 15 years. The number of publications increased from about 600 in 2000 to more than 8000 in 2016.

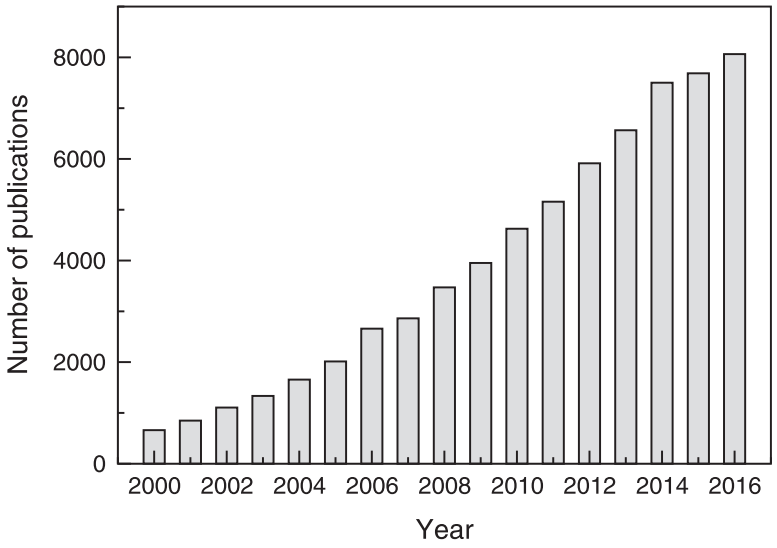

Figure 1.1: Number of publications with the term 'ionic liquids' since 2000. Results from Web of Science (04/07/2017).

Due to some unique properties that differ from usual solvents, ionic liquids found their way into applications in almost every single branch of physical and chemical science. They are characterized e.g., by a low vapour pressure at room temperature and a large liquid range up to more than 300 K. [18] These features support their usage as alternative solvents in synthesis and catalysis. [19] Furthermore, some ionic liquids show a large electrochemical window up to 5 V. [20] That is why they can be used for several electrochemical applications, like Li-ion batteries [21], fuel cells [22,23] and solar cells [24]. Additionally, ILs are deployed as lubricant fluid [25,26], as operating fluid in high pressure processes [27] as well as in extraction or refinement processes [28–30]. During the last years even applications like gas absorption material, refrigerant and CO_2 sensor [31] as well as liquid mirror telescopes [32] and active pharmaceutical ingredients [33] were added. A mentionable fact is that ionic liquids were selected as the most important British innovation of the 21st century by the Great British Innovation Vote. [34]
Despite all these various possible applications, only a few of them are implemented on an industrial scale. The first was a biphasic catalytic process, the DIFASOL process, developed by the Institut Français du Pétrole (IFP), for the dimerization of butenes into a mixture of low-branched octenes. [35] Later in 2002, the BASIL™ process of the BASF company, which is used for the production of photoinitiators like Lucirin®, was introduced. [36,37] In 2015, the working group of Ken Seddon presented an ionic liquid process for mercury removal from natural gas and demonstrated it on an industrial scale. [38]

For further industrial application the detailed knowledge of physical and chemical properties of the ionic liquids is very important. These properties are strongly influenced by the intermolecular interactions in ILs. These interactions can differ especially between two classes of ionic liquids, namely protic (PILs) and aprotic (APILs) ionic liquids. The first group is prepared through the stoichiometric neutralization reaction of certain Brønsted acids and Brønsted bases. Thus, a key feature of these PILs is that they have an available labile proton on the cation, allowing the formation of strong hydrogen bonds to the anion. [39] But describing the subtle energy balance between Coulombic interaction, hydrogen bonding and dispersion forces [40,41] that are all present in ionic liquids, is still a challenge.

1.2 Interactions in ionic liquids

As mentioned in the previous section, ionic liquids consist solely of cations and anions. They can participate in a variety of attractive interactions ranging from strong forces like Coulomb interactions over specific and anisotropic forces like hydrogen bonding [42] and halogen bonding [43] to weak nonspecific and isotropic forces like Van der Waals [44], e.g., dispersion forces [45]. All of them have their own characteristic influence on the transport and thermodynamic properties of the ionic liquids. In the following chapter mainly the subtle energy balance between Coulomb interaction, hydrogen bonding and dispersion forces should be discussed.

Ion pair concept

Like charges repulse, while opposite charges attract each other. That is a fundamental principle in physics. [46] In electrolyte solutions this is picked up by the ion pair concept firstly introduced for strong electrolytes by Bjerrum in 1926. He proposed the idea of a pair of oppositely charged ions dispersed in water behaving as one unit. [47] Although ionic liquids do not fit perfectly to this concept based on infinite dilution, the ion pair itself is known as the smallest representative unit of ILs that simulates their structural as well as their binding features. Thus, it has been widely employed to model physical and chemical properties and liquid phase behavior of RTILs. [48–50]
Experimentally the ion pairs have been proven to exist in the liquid phase by methods like conductivity, NMR, and X-ray studies. [51–55] For the solution phase further techniques, like mass spectrometry, dielectric spectroscopy and IR spectroscopy were used. [56–69] Far infrared measurements from Fumino et al. indicated in 2013 the presence of exclusively

contact ion pair (CIP) species in the pure IL triethylammonium iodide, that even stay intact in solution with $CDCl_3$. Only in mixture with more polar solvents like DMSO some of the CIPs are transferred to solvent separated ion pairs (SIPs). [70] Many ionic liquids are also known to evaporate as ion pairs, [71, 72] which also suggest that they may be present in the bulk phase.
The main contribution of the interaction within those ion pairs was undoubtedly assigned to electrostatic forces. The strong anion-cation interaction in these Coulomb fluids is characterized by extremely low vapour pressures as well as high enthalpies of vaporization. [19, 39, 73–78] But during the last decade, several research groups worked on identifying the extent of contributions from other fundamental forces to energetics of ionic liquids. [40, 79–83] A particular emphasis was given to quantifying hydrogen bonding and dispersion forces.

Hydrogen bonding and dispersion forces

For the potential formation of hydrogen bonds in ionic liquids the cation should contain labile H-atoms as they are present e.g., in ammonium- or imidazolium-based ones. On the other hand, the anion should provide a lone pair of electrons as in the case of tetrafluoroborate or bis(trifluoromethylsufonyl)imide. If this requirement is fulfilled, the cation is the H-bond donor and the anion is the H-bond acceptor. Based on the cation it can be distinguished between strong hydrogen bonds in protic ionic liquids and weaker or no hydrogen bonds in aprotic ionic liquids. [84] The additional interaction often imposes a high degree of directionality to the ion pair formation [71, 85] and becomes consequently a secondary structure-directing contributor. To differentiate the IL H-bond from the already well established ionic H-bond, Hunt et al. introduced the hydrogen bond between two ionic species as the doubly ionic H-bond. [84]
A variety of working groups could show that attractive interaction within the ion pair can be enhanced by the formation of those doubly ionic H-bonds. The same is true for additional dispersion forces. In 2016, Zaitsau et al. used vaporization enthalpies, far-infrared spectroscopy and dispersion-corrected calculations to dissect the interaction energies between cations and anions in aprotic and in protic ionic liquids. It was found that the higher total interaction energy in PILs results from the strong and directional hydrogen bonds between cation and anion, whereas the larger vaporization enthalpies of AILs clearly arise from increasing dispersion forces between ion pairs. [72] Ludwig showed in a theoretical work by means of dispersion-corrected DFT calculations that the dispersion forces can even be as strong as the hydrogen bonds in PILs. [86] Both energies could be quantified to be about $50\,kJ\,mol^{-1}$, each representing ten percent of the overall interaction

energy. Additionally, the dispersion interaction could be dissected into two portions. One third could be related to the dispersion interaction within an ion pair, enhancing the H-bond strength, two thirds stem from dispersion interaction between the ion pairs. By combining far infrared spectroscopy and dispersion-corrected DFT-calculations, Fumino et al. could even prove a temperature-dependent transition from hydrogen bonding to dispersion-dominated interaction between anions and cations in the PIL trihexylammonium triflate. [87]
To summarize, it can be pointed out that hydrogen bonds and dispersion forces are two of the molecular features that clearly determine the properties of Coulomb-dominated ionic liquids. [88,89] But despite all new insights, the attractive interaction seems to be limited to oppositely charged ions. Short-range directional attractive interactions between ions of like charge in ionic liquids seem to be an elusive concept without any spectroscopic evidence so far.

1.3 Attraction between ions of like charge

Whereas the concept of pairing between ions of opposite charge is well accepted, the association of like-charged ions seems to be a counterintuitive phenomenon. Nevertheless, there are several works in literature dealing with the evidence for this elusive concept. Holz and Patil published already in 1991 attractive interaction in aqueous salt solutions of K/CsBr. [90] Only some years later, Larsen and Grier published a work about the like charge attraction in metastable colloidal crystallites. [91] 2003 Benrraou et al. found the same for the micellation of tetraalkylammonium surfacants [92] and 2013 Shih et al. presented attractive interaction between guanidinium ions in water. [93] Most recently, Gamrad et al. reported self association of simple organic cations based on hydrogen bonding. Cation-cation pairing was detected in crystal structures as observed in the X-ray structure. [94] All of these systems have in common that the interaction between like-charged ions requires the mediation of solvent molecules, usually water. Furthermore, like-charge attraction is also reported for larger biomolecular structures like oligopeptides and DNA. [95,96]
Three works even deal with this topic in ionic liquids. Mele could measure Nuclear Overhauser Effect (NOE) contacts between protons of imidazolium cations in aprotic ionic liquids. There were some information about the distance, but no evidence for the type or the strength of the interaction. [97] However, these results were challenged by Steinhauser et al. [98,99] They argued that Mele's analysis was only taken in the spirit of intramolecular NOE and thus ignores the intermolecular part which is strongly influenced by the

dynamics of the spin-pairs. The second and third work about ionic liquids by Fakhraee et al. [100] and Katsyuba et al. [101] were based on molecular dynamics simulation and ab initio calculations, respectively. The authors investigated the influence of hydroxyl functional groups on the structural properties of different ionic liquids and found attractive cation-cation interaction via hydrogen bonding in those ILs with bulky anions, like NTf_2^- and PF_6^-.
To summarize, so far like-charge attraction was only reported for large-scale structures, assemblies, stabilizing frameworks or aqueous solution, wherein mediating water molecules play an important role. But there is no experimental evidence for the attraction between like-charged ions in ionic liquids.

2 Aim of this Work

Ionic liquids as salts composed solely of ions are remarkable liquids. Their unique and fascinating properties offer a wide range of opportunities for science and technology. New combinations of ions provide changing physical properties and thus novel potential applications for this class of liquid materials. To a large extent, the structure and properties of ionic liquids are determined by the intermolecular interaction between the ions. Therefore, an understanding of chemical bonding and intermolecular forces is one of the major topics in the IL community. In common ionic liquids especially the anion cation interaction is discussed and the concept of cation-anion pairing is well characterized. It is known that the ion pair itself is the smallest representative unit of ionic liquids that simulates their structural as well as binding features. It has widely been employed to model physicochemical properties and liquid behavior of RTILs. But currently the attractive cation-cation interaction remains an elusive concept. So far there is no proper spectroscopic evidence for attractive interactions between ions of like charge in ionic liquids.
Thus, the aim of this work is to prove and to systematically investigate this counterintuitive phenomenon by means of IR- and NMR-spectroscopy combined with theoretical methods like DFT and NBO analysis. Especially the following questions should be answered:

- What is the nature of the attractive intermolecular interaction between the cations?
- Are there differently sized cationic clusters in the ionic liquid?
- What is the largest size of a cationic cluster in the liquid phase?
- Is the equilibrium between different types of H-bonded species (c-a and c-c) dependent on temperature?
- What is the influence of OH density on the cationic cluster formation?
- Is the cationic cluster formation dependent on features like size, shape and charge delocalisation of the ions?

- Are cationic clusters also observable in the gas phase and in the solid state?

All these questions should be answered with a combination of experimental (IR, NMR) and theoretical (DFT, NBO) methods. But analysing non-covalent interactions in liquids is still a challenge. This is in particular true for ionic liquids with their special energy balance between different types of intermolecular interactions. Since the cation-cation interaction is based on hydrogen bonding motifs between these cations, especially the OH-stretching region in the IR spectra will be evaluated. By deconvoluting the spectra different cationic clusters should be indentified. Quantum chemical calculations should be used to assign the spectroscopic signatures to concrete configurations and to analyze the H-bond network with respect to cooperative effects as they are known for molecular solvents like water or alcohols.
Concluding this work, quantum chemical calculations of the gas phase should answer the question whether differently charged cationic clusters can also be observed experimentally in the gas phase. Two different strategies on how to convert the cationic clusters from the kinetically into the thermodynamically stable regime will be presented and compared. These investigations should be a promising starting point for further research in the field of like-charge attraction in ionic liquids.

3 Results and Discussion

The motivation, results and highlights of **publications I-V** are summarized in this chapter. All discussions are done in comparison with the existing literature. **Publication I** describes for the first time the counterintuitive phenomenon of cluster formation between ions of like charge in ionic liquids for an hydrogen bound cationic dimer. In **publication II** even larger clusters up to cyclic tetramers are described. The phenomenon is discussed as a function of OH density in **publication III** and as a function of the anion interaction strength in **publication IV**. Finally, a theoretical approach of stabilizing the cationic cluster network by either neutral molecules or negatively charged counterions is presented in **publication V**. This work should be the basis for further investigations in the gas phase.

3.1 The first cationic dimer

The attractive interaction between like-charged cations was observed for the first time with mid-infrared measurements of the ionic liquid (2-hydroxyethyl)-trimethylammonium bis(trifluoromethylsufonyl)imide (**Publication I**). The cation is also known as cholinium $[Ch]^+$ and, combined with chloride as counterion, forms choline, which is a water-soluble vitamin-like substance and of relevance in biochemical processes, especially in brain and memory development. [102] Together with the $[NTf_2]^-$ anion the melting point is lowered to 300 K [103], so that an ionic liquid $[Ch][NTf_2]$ is formed. The most characteristic feature of the cholinium cation is the hydroxyl group that is known for the formation of hydrogen bonds as they are present in molecular solvents like water or alcohols. [104–108] On the other hand also the sulfonyl groups of the $[NTf_2]^-$ anion are suitable hydrogen bond acceptors, leading to an expected situation of H-bond-enhanced attractive electrostatic interaction between the cation and the anion as it is known for a lot of ionic liquids. [109–114]
To study the hydrogen bond characteristics temperature dependent mid-infrared measurements have been done. The OH stretching region of the spectra is presented in figure 3.1. Quite different from the expectation, the OH contribution is not very symmetric,

indicating that there have to be present different configurations of the hydroxyl group in the ionic liquid. Overall, the spectra can be deconvoluted into four different contributions. For all measured temperatures the deconvolution can be found in the **supporting information of publication I**. For a temperature of 323 K the largest vibrational intensity at 3541 cm^{-1} can be referred to an attractive OH$\cdots$OS hydrogen bond between the cation and the anion. The redshifted contributions at 3474 cm^{-1} and 3431 cm^{-1} indicate OH$\cdots$OH hydrogen bonding between two cholinium cations. This interpretation is supported by DFT-D3 calculations using the B3LYP functional in Gaussian09 with the split valence basis set 6-31+G* including polarization and diffuse functions as well as dispersion correction D3. The calculated structures are shown in figure 3.2. It is obvious that two different types of intermolecular interactions, especially two types of H-bonds are present in this ionic liquid. First, there are anion-cation pairs characterized by OH$\cdots$OS hydrogen bonding and secondly, attractive cation-cation interaction via OH$\cdots$OH hydrogen bonds can be observed. So far, this is the first spectroscopic evidence for directional cation-cation interaction via hydrogen bonding in ionic liquids.
It is interesting to note that the redshift between the vibrational bands of the ion pair and the cation dimer in the [Ch][NTf_2] is about 110 cm^{-1}. In comparison, the redshift between an ethanol monomer and dimer is 112 cm^{-1}. The molecular structure of the ethanol molecule is similar to that of the hydroxyethyl functional group of the cholinium cation. In figure 4 of **publication I** the mid infrared spectra for both liquids are presented. The OH band of the ethanol monomer is brought in line with the main OH band of the cholinium and finally the spectra look very similar and show the same frequency shifts for the cation dimer and the ethanol dimer. That means the hydrogen bond strength between the cations is in the order of that found for molecular liquids like alcohols. [104–108]
To sum up, this is the first example of attractive hydrogen bonds in liquid phase overcoming repulsive Coulombic interaction without any solvent mediation.

3.2 Strategy to support cationic cluster formation

Based on the these interesting findings, a strategy for supporting and studying the formation of cationic clusters systematically was developed. In this process especially two issues are relevant. Firstly, how should the molecular structure of the ionic liquid look like in order to increase the possibility for attractive hydrogen bonding between the cations? And secondly, which experimental and theoretical methods are useful to investigate such counterintuitive phenomenon? Both questions are discussed in the following two sections.

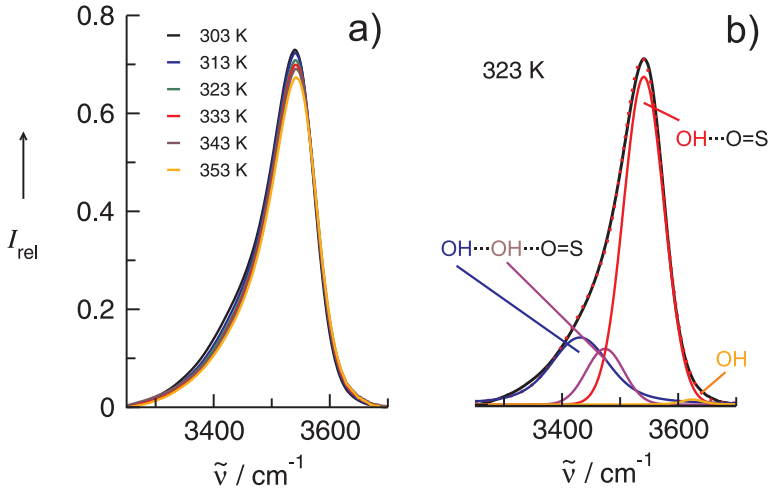

Figure 3.1: Mid-infrared spectra of the OH stretching region of the ionic liquid [Ch][NTf_2]
a) in the temperature range between 303 and 353 K and
b) at 323 K deconvoluted into four different contributions.

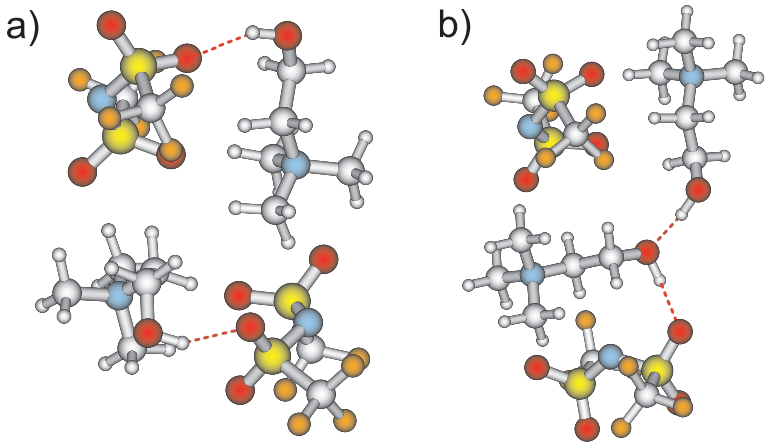

Figure 3.2: B3LYP-D3/6-31+G* calculated structures for the ionic liquid [Ch][NTf_2]
a) cation-anion pairs characterized by OH···OS hydrogen bonds and
b) additional cation-cation interaction resulting in cooperative OH···OH···OS hydrogen bonds.

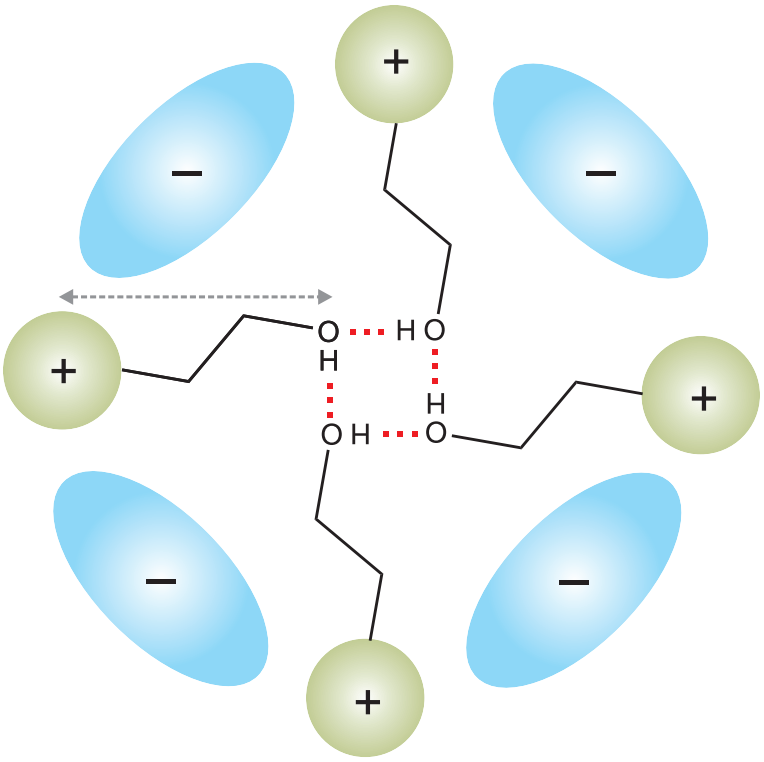

Figure 3.3: Supporting the cationic cluster formation in ionic liquids with I) the introduction of hydroxyl groups for hydrogen bonding, II) the use of weakly coordinating anions and III) increasing the distance between the hydroxyl groups and the center of positive charge of the cation.

3.2.1 Changing the molecular structure

For supporting the cationic cluster formation in ionic liquids mainly three aspects of the molecular structure are of relevance. First, and most important, it is necessary to introduce hydroxyl groups for possible hydrogen bonding into the system. Based on the results of the $[Ch][NTf_2]$, this was realized with functional groups at the cation. Secondly, to overcome the repulsive forces between the cations only weakly coordinating anions were chosen as counterions and finally, the distance between the positive charge center and the functional hydroxyl group should be large enough, realized by the introduction of an alkyl chain. This way the functional group could behave comparable to its neutral equivalent and the impact of the positive charge on the hydrogen bonding is minor. [84] In figure 3.3 this strategy is presented on the general example of a cyclic tetramer. Taking all these aspects into account, the question should be answered, whether there are other combinations of cations and anions that maybe show more and larger cationic clusters than the IL $[Ch][NTf_2]$. Therefore, the cation was changed from $[Ch]^+$, with a located positive

charge at the nitrogen, into 1-(2-hydroxyethyl)-3-methylimidazolium $[HEMIm]^+$, which is characterized by a delocalized positive charge in the aromatic ringsystem. The charge delocalization further increases the distance between the OH group and the positive charge center and leads to a completely other binding situation in general. Additionally, the anion was changed from $[NTf_2]^-$ into tetrafluoroborate $[BF_4]^-$. The interaction strength of both anions is similar, but $[BF_4]^-$ is more spherical, forming hydrogen bonds that are much less directed, compared to the $[NTf_2]^-$. Combining both ions the ionic liquid $[HEMIm][BF_4]$ is formed and will be discussed below.

$[HEMIm][BF_4]$

For $[HEMIm][BF_4]$ the OH stretching region of the mid infrared spectra has been evaluated for different temperatures (**Publication II and III**) and is presented in figure 3.4 on the left. At lower wavenumbers significant additional contributions grow with decreasing temperature. The most redshifted OH contributions of this ionic liquid even range into the CH vibrational contributions. Thus, it is necessary to make sure that all the intensity in the frequency range between 3200 and 3600 cm^{-1} is really originating from OH stretching vibrations and not from overtones, combination bands or contributions of other molecule groups. Therefore, two different experiments, based on diluting and deuterating the OH position, are done.

First, the effect of decreasing the OH density on the cationic cluster formation should be discussed. This is presented in detail in **publication III**. One can imagine that the cationic cluster formation is dependent on the number of interaction sites in the bulk phase. Considering that the attractive interaction between the cations is based on hydrogen bonding, especially the number of OH groups is important. To investigate this effect systematically, the ionic liquid $[HEMIm][BF_4]$ is mixed with $[PMIm][BF_4]$ in different concentrations. This way the OH group of the cation is replaced with a methyl group, which is not able to form hydrogen bonds. Figure 3.4 on the right presents the OH stretching region of the IR spectra for different concentrations (100, 75, 50, 25, 10 mol%) of $[HEMIm][BF_4]$ in $[PMIm][BF_4]$ at a low temperature of 213 K. The deconvolution of these spectra can be found in the **supporting information of publication III**. Obviously the overall intensity increases with increasing OH density. Even so, the c-a vibrational band at 3454 cm^{-1} does not increase linearly but rather loses intensity in favor of the strongly enhanced redshifted vibrational bands at lower wavenumbers. At the lowest concentration of 10 mol% the density of the OH functional group is extremely low and should not allow any formation of OH$\cdots$OH bounded cation-cation clusters. This is reflected in the remaining small but symmetric OH contribution at 3545 cm^{-1} and leads to the conclusion

that at a concentration of 10 mol% most of the hydrogen bonds are formed within anion-cation pairs and cationic cluster formation is nearly suppressed.
For further estimation the OH contributions should be separated from the CH contributions. Therefore, the OH position of [HEMIm][BF_4] was deuterated, leading to a shift of all the OH contributions between 3200 and 3600 cm^{-1} down to the OD region between 2300 and 2700 cm^{-1}, which doesn't show any signals for the protonated ionic liquid. Both spectra are shown in figure 3.5 for the same frequency range. This experiment is a further proof for the fact that all the contributions in the published spectra can not be anything other than OH vibrations. Overtones, combination bands and contributions of other molecule groups can be excluded this way. Additionally, the spectra of the deuterated IL are used to subtract them from the spectra of the protonated form. Getting rid of all oberlapping CH contributions, the OH vibrational modes can be better evaluated.
The difference spectra are shown in figure 3.4 on the left. They can be deconvoluted into four different contributions, shown in figure 3.6 for a temperature of 233 K. The deconvolution for all other temperatures can be found in the **supporting information of publication II**. The main vibrational band at 3547 cm^{-1} can be assigned to the OH$\cdots$BF hydrogen bond between the cation and the anion. The high wavenumber indicates that the cation-anion hydrogen bond is relatively weak, comparable to the interaction strength of water or methanol in similar ionic liquids. [115,116] The cation dimer, that is also present in the [Ch][NTf_2], is located at 3496 cm^{-1}. But only these two structural motifs are not enough to describe the whole experimental spectrum. The two additional contributions in the lower frequency range can be assigned to even larger hydrogen bonded clusters between the $[HEMIm]^+$ cations. In this ionic liquid also linear trimers and tetramers (3402 cm^{-1}) as well as cyclic tetramers (3286 cm^{-1}) are present, while the linear structures can not be resolved spectroscopically anymore (see figure 3 of **publication II**). The experimental findings are supported by DFT-D3/6-31+G* calculations on differently-sized ion pair clusters including opposite charge and like charge attraction. As an example the calculated structures of possible tetrameric configurations are shown in figure 3.7. Those kind of linear and cyclic clusters are known for molecular solvents like water or alcohols. They are stabilized by increasing cooperative effects with increasing clusters size, affecting different spectroscopic and molecular properties, which will be discussed in the following chapter 3.2.2. The most stable cyclic tetramer represents a cluster with a plus four net charge. Obviously the amount and the size of the cationic clusters are strongly dependent on the molecular structure of the ionic liquid. Here mainly three aspects are important. The first one is the interaction strength of the anion. This dependence will be discussed in more detail in chapter 3.3. Two other important points for the cluster

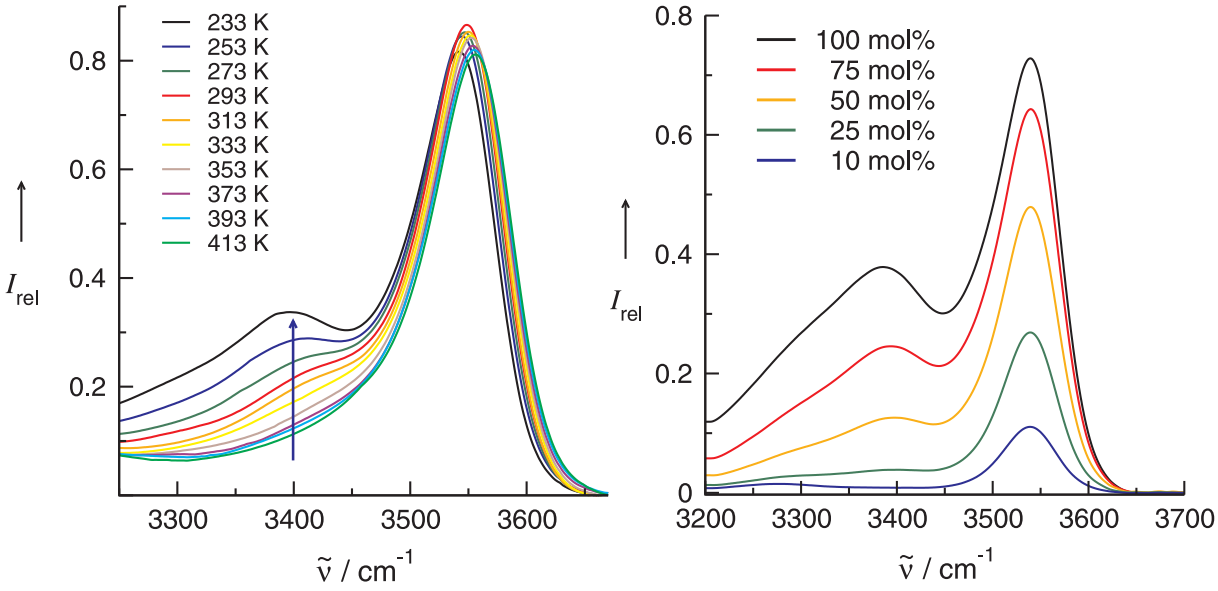

Figure 3.4: Mid-infrared spectra of the OH stretching region of the ionic liquid [HEMIm][BF_4] for different temperatures (left) and for different concentrations at 213 K (right).

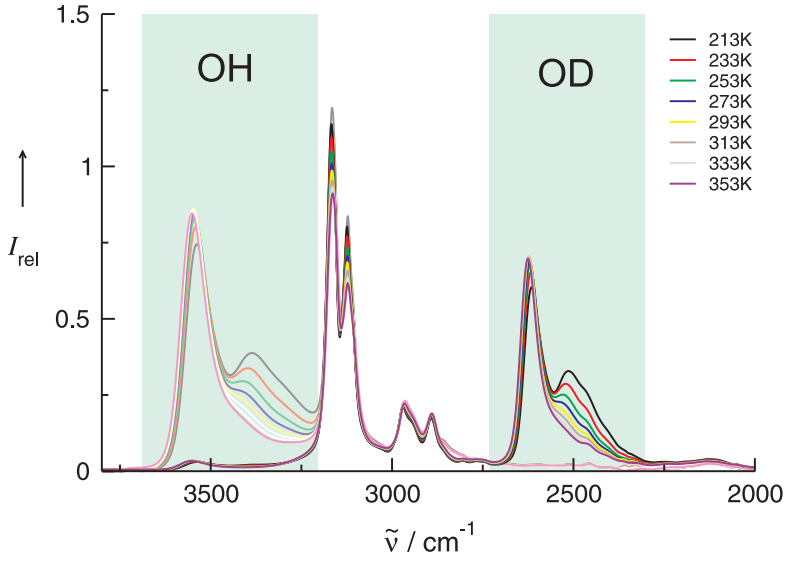

Figure 3.5: Mid-infrared spectra of the ionic liquid [HEMIm][BF_4] for the OH protonated form (light colors) and for the OD deuterated form (intense colors).

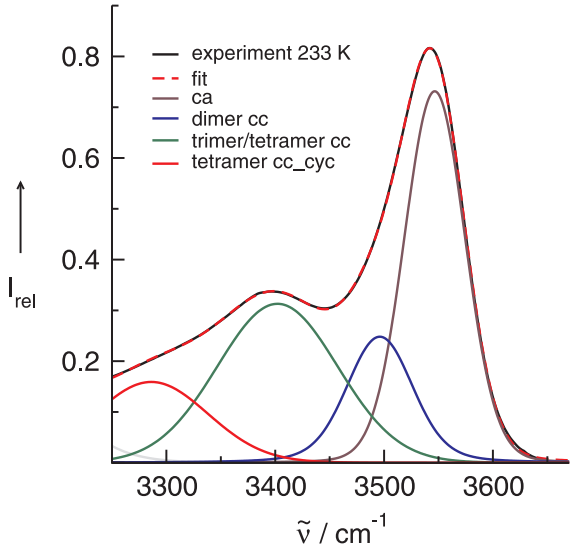

Figure 3.6: Mid-infrared spectrum of the ionic liquid [HEMIm][BF_4] at 233 K deconvoluted into four contributions.

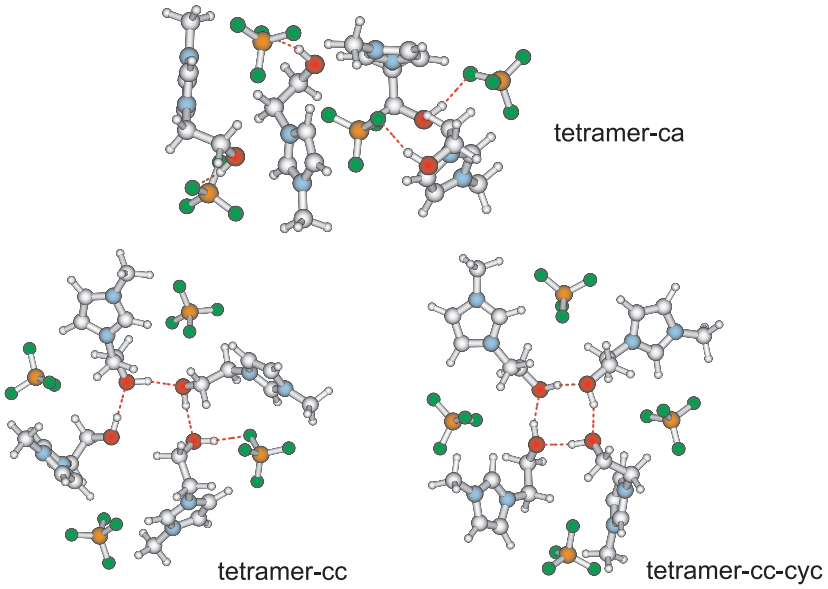

Figure 3.7: B3LYP-D3/6-31+G* calculated structures for different configurations of cationic tetramers that are present in the ionic liquid [HEMIm][BF_4]

formation are the structure of the cation and the length of the hydroxyalkyl chain at the cation. Both dependencies are not included in this work because they are part of currently ongoing investigations.

3.2.2 Suitable Methods

Short introduction and motivation

In this chapter it should be discussed which theoretical and experimental methods are useful to study the cluster formation between cations in ionic liquids systematically. Since the like-charge attraction is based on hydrogen bonding, especially methods that are sensitive for intermolecular interaction strengths are needed. In this respect for example, quantum chemical calculations combined with NBO analysis as well as IR and NMR spectroscopy are powerful tools. Only by a combination of both, theory and experiment, it is possible to describe the nature of the cationic clusters in detail.

Mid-infrared spectroscopy

Since the cationic cluster formation in OH-functionalized ionic liquids is based on attractive hydrogen bonding between the OH groups of the cations, especially the OH stretching region of the mid-infrared spectra is filled with important information. As it is shown in figures 3.1 and 3.6, different configurations of the OH group are represented by different contributions in the spectra or at least by a shoulder. Nevertheless, it is only possible to decide whether there are one or more configurations present in the ionic liquid. It is impossible to define the concrete configurations that result in the experimental spectra. Therefore, additional methods like quantum chemical calculations are necessary.
Furthermore, the position of the OH contribution provides information about the interaction strength of the hydrogen bond. For the two introduced ionic liquids the c-a contributions, for example, are located at 3541 cm^{-1} for [Ch][NTf_2] and 3553 cm^{-1} for [HEMIm][BF_4], at a common temperature of 313 K. Since the interaction strength is mainly influenced by the anion, these values reflect the similar interaction strength of [NTf_2]$^-$ and [BF_4]$^-$. However, the c-c contributions are always redshifted to lower wavenumbers in comparison to the c-a contributions, indicating that the hydrogen bonds within the ion pairs are weaker than those within the cationic clusters. This way, the position of the OH contributions support the explanation that cationic clusters are stabilized by cooperative effects.

Quantum chemical calculations

Quantum chemical calculations are a powerful tool for the description of intermolecular interactions in general and hydrogen bonding in particular. Furthermore, it can be used for the prediction of energetic, physical and spectroscopic properties of ionic liquids. [34] In this work, all the calculations have been performed with the Gaussian09 program using the B3LYP-D3/6-31+G* method. The small, but well-balanced 6-31+G* basis set includes polarization as well as diffuse functions and has been shown to be suitable for calculating hydrogen bonded clusters of like-charged ions in all the **publications I-V**. In the following, data of **publications I, II** and **V** has been rearranged in order to make it comparable for both introduced ionic liquids [Ch][NTf_2] and [HEMIm][BF_4]. Especially three different properties, namely IR frequencies $\tilde{\nu}_{OH}$, proton chemical shifts δ^1H as well as intra- R(OH) and intermolecular R(O$\cdots$H) / R(O$\cdots$O) bond distances will be discussed. In all cases, the data for a dimer, a linear trimer and a cyclic tetramer is plotted related to the monomer species. Due to the fact that similar behavior can be expected for alcohols, the data of [Ch][NTf_2] will be compared with DM1B and that of [HEMIm][BF_4] with n-propanol.
By calculating the IR frequencies, the experimental findings of the deconvolutions can be confirmed. This is shown in figure 3.8. For both ILs the calculated IR frequencies of the pure cationic clusters are plotted as red squares. They are obviously redshifted compared to the monomer species, indicating the increasing strength of the hydrogen bonds with increasing cationic cluster size. While for [Ch][NTf_2] the values seem to be saturated starting with the dimer, the redshift for [HEMIm][BF_4] increases systematically until the cationic cyclic tetramer. The same has been found in the experiment. While the cationic dimer in [Ch][NTf_2] was only represented by a shoulder in the MIR spectrum, the larger clusters in [HEMIm][BF_4] lead to well separated additional contributions. The experimentally obtained frequencies are included in figure 3.8 as grey dashed bars. In both cases the corresponding alcohols, plotted as blue circles, show similar behavior. But maybe more important than confirming the experimental results, are the additional information that can be derived by this method. By calculating the IR frequencies, the experimental contributions can be related to concrete configurations like shown in figures 3.2 and 3.7. Furthermore, it is possible to calculate the proton chemical shifts δ^1H of the OH groups as it is shown in figure 3.9. They are strongly shifted downfield with increasing cationic cluster size compared to the monomer. Obviously, the stronger hydrogen bonded clusters result in a deshielding of the hydroxyl group. This is true for both ILs as well as for the alcohols and should be also experimentally observable in the liquid phase. A molecular property that is sensitive for intermolecular interactions like hydrogen bonds are the bond

distances. The calculated values are presented in figure 3.10. As expected, the intramolecular bond lengths $R(\mathrm{OH})$ increase while the intermolecular bond distances $R(\mathrm{O}\cdots\mathrm{H})$ and $R(\mathrm{O}\cdots\mathrm{O})$ decrease with increasing cluster size, respectively. This behavior confirms the increasing strength of hydrogen bonding with increasing cluster size.

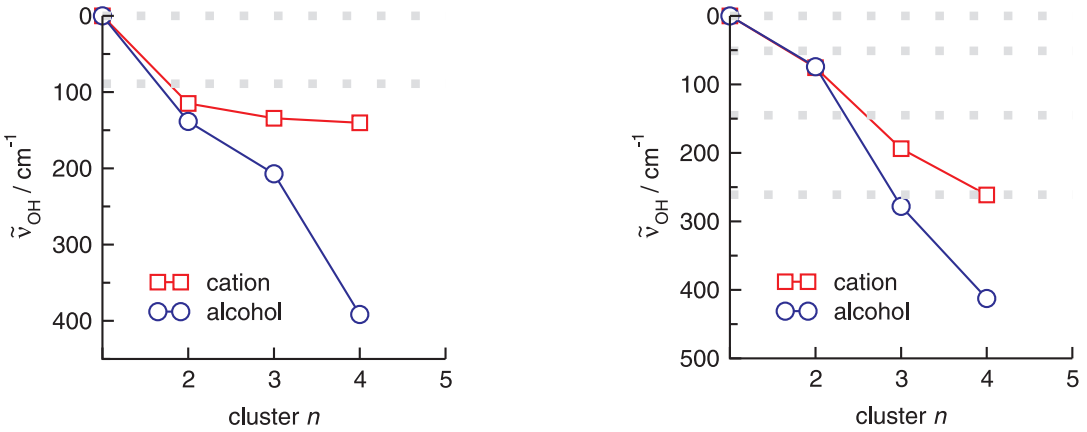

Figure 3.8: B3LYP-D3/6-31+G* calculated IR frequencies $\tilde{\nu}_{\mathrm{OH}}$ for [Ch][NTf_2] and DM1B (left) and for [HEMIm][BF_4] and n-propanol (right).

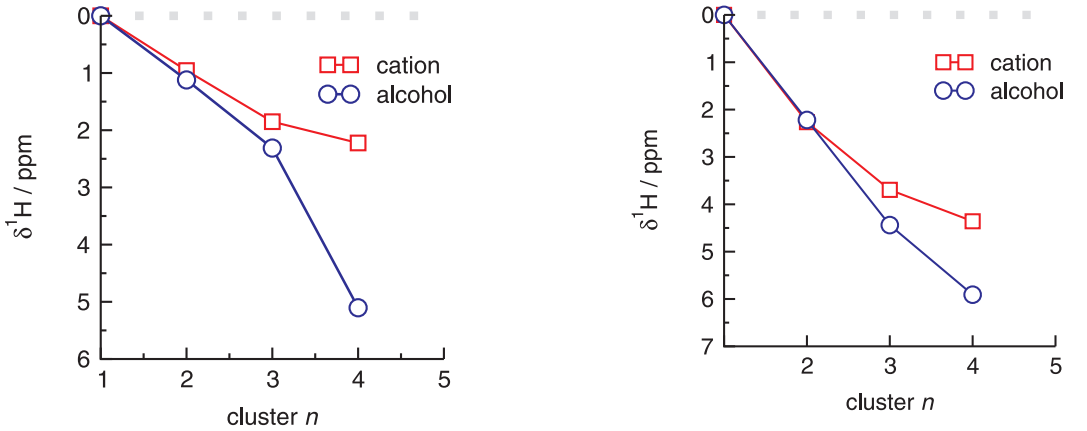

Figure 3.9: B3LYP-D3/6-31+G* calculated proton chemical shifts δ^1H for [Ch][NTf_2] and DM1B (left) and for [HEMIm][BF_4] and n-propanol (right).

Of course this is not a complete list of properties that are able to be calculated with quantum chemical calculations. For example, it is also possible to evaluate binding energies per species, which could be used to discuss the question of thermodynamic or kinetic stability. These results are summarized in **publication V** and will be discussed in chapter 3.4 in detail. But as a conclusion, all three discussed properties confirm the

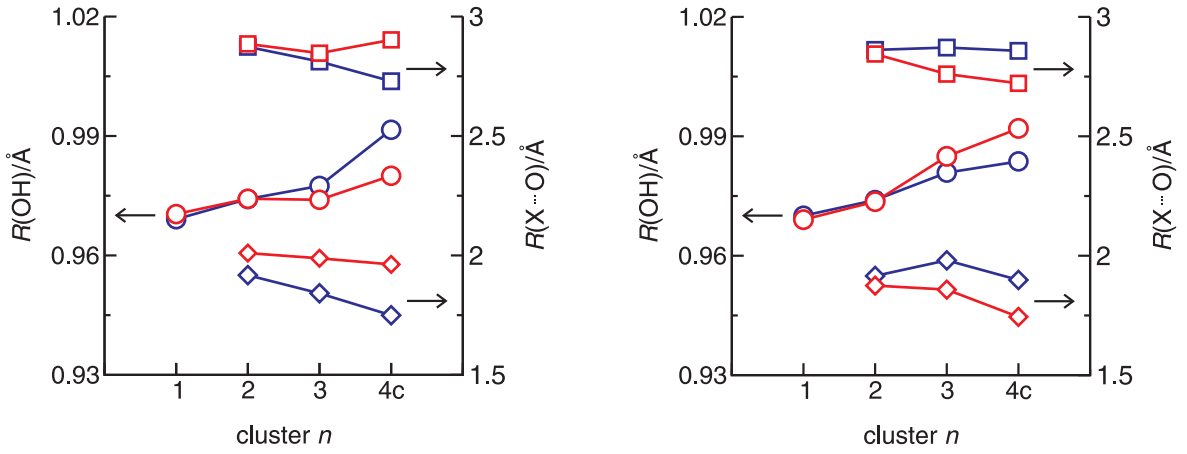

Figure 3.10: B3LYP-D3/6-31+G* intramolecular bond lengths R(OH) as well as intermolecular bond distances R(H···O) and R(O···O) for [Ch][NTf_2] (left) and for [HEMIm][BF_4] (right).

increasing strength of hydrogen bonding with increasing cluster size and therefore support the concept of cooperative effects.

NBO analysis

As mentioned in the previous section, DFT calculations are able to describe the cationic cluster formation. A lot of different properties indicate that the attractive hydrogen bonding between the cations is based on cooperative effects. [107, 108] This phenomenon is based on a charge transfer from the oxygen lone pair orbital of the first cation to the OH antibond orbital of a second cation, leading to larger electron density that can be further transferred into the OH antibond orbital of a third cation, etc. This way, the hydrogen bonding is enhanced stepwise. The charge transfer q_{CT} as well as the second order stabilization energies $\Delta E(2)_{n\rightarrow\sigma^*}$ can be calculated by analyzing the DFT calculations with the NBO 6.0 program. [117, 118] In figure 3.11 both properties are plotted versus the experimentally obtained IR frequencies. The IR redshifts of growing cluster size obviously go along with increasing charge transfer q_{CT} as well as increasing second order stabilization energies $\Delta E(2)_{n\rightarrow\sigma^*}$. The almost linear behavior indicates that both properties characterize hydrogen bonding and the cooperativity in a similar way. The same behavior can be found for the correlation of the NBO parameters plotted versus the proton chemical shifts (figure 7 of **publication V**). Obviously, the attractive hydrogen bonds between the cations in the described ionic liquids are comparable to the 'anti-electrostatic' hydrogen bonds (AEHB) Klein and Weinhold claimed for doubly charged [A-HB]$^{\pm}$ complexes, wherein the short-range donor-acceptor covalency forces overcome

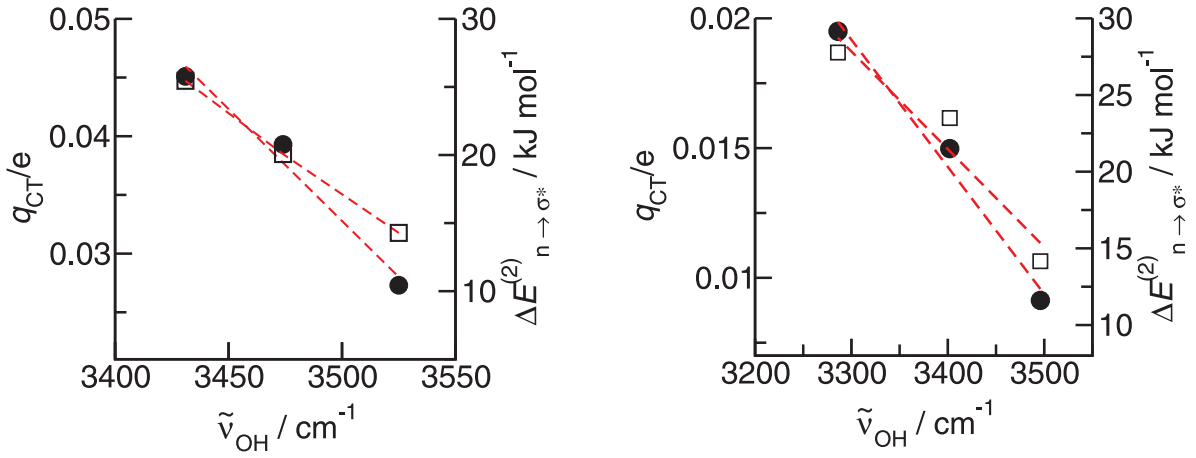

Figure 3.11: NBO calculated 2nd order stabilization energies $\Delta E(2)_{n\rightarrow\sigma^*}$ and estimated total charge transfer q_{CT} plotted versus measured IR frequencies $\tilde{\nu}_{OH}$ for [Ch][NTf_2] (left) and for [HEMIm][BF_4] (right).

the powerful long-range electrostatic forces. [119, 120]
Nevertheless, it has be to mentioned that there is a vital discussion in literature about the utility of the NBO concept. As Stone reported recently, the main point of criticism is that the NBO properties are strongly overestimated, leading to a wrong description of the nature of hydrogen bonds, which are not dominated by the charge transfer energy in his point of view. [121] The most popular alternative to the NBO concept is the energy decomposition analysis (EDA). [122, 123] This method is also able to quantify intermolecular bonds by decomposing the calculated interaction energy into as many interpretable contributions as possible, including ,e.g. permanent and induced electrostatics, dispersion and charge transfer. [124] But it is computationally expansive. For that reason it has not been applied to structures larger than dimers. Thus, a discussion of cooperativity based on EDA is delicate so far.
From this point, of view the NBO concept is a good opportunity to show the correlation as well as the complementary nature of theoretically available NBO parameters and experimentally available spectroscopic observables.

NMR spectroscopy

As shown by the DFT calculations, also proton chemical shifts are sensitive for the strength of hydrogen bonding. Therefore, cationic cluster formation should be indicated by downfield shifts of the proton chemical shifts of the hydroxyl groups. The problem with measuring this downfield shift experimentally, is that NMR spectroscopy is a slow

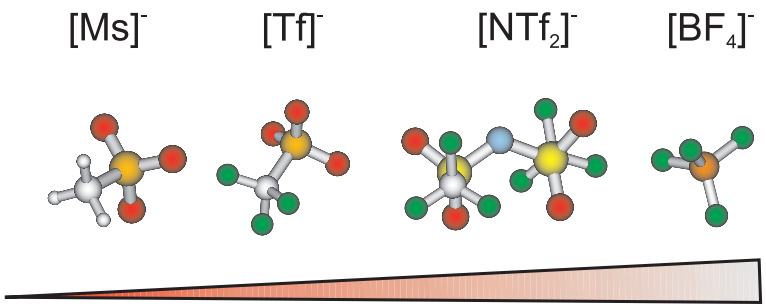

Figure 3.12: Molecular structure of four different anions arranged in the direction of increasing interaction potential.

method. Compared to IR spectroscopy, where both cluster species (c-a and c-c) can be observed separately from each other, in NMR spectroscopy only time-averaged properties can be measured. Distinct configurations or binding motifs of the OH group at the cation can not be addressed. Instead, only one single average signal for all the OH groups present in the ionic liquid is found. Still, it should be possible to detect the cationic cluster formation by NMR spectroscopy using a simple trick of comparing the temperature behavior of a cluster-forming ionic liquid with that of a non-cluster-forming ionic liquid. In the case of attractive hydrogen bonding between the cations, the downfield shift of the proton chemical shift with decreasing temperature should be much larger than that found in an ionic liquid consisting only of cation-anion pairs. This way, the change in equilibrium between the c-a pairs and c-c clusters is reflected. A detailed description and an example for this experiment can be found in the next chapter (figure 3.14).

3.3 Anion Dependence

One fundamental requirement for the formation of cationic clusters in ionic liquids is lowering the attractive Coulombic interaction within the ion pair by choosing weakly coordinating anions. This way, alternative attractive interactions like hydrogen bonding are promoted. This chapter should summarize especially the dependence of the cluster formation on the interaction strength of the anion (**publication IV**). Hereunto, the IR spectra of four different ionic liquids sharing the same $[HEMIm]^+$ cation, but different anions, have been measured. The interaction strength increases in the direction $[BF_4]^- \approx [NTf_2]^- < [Tf]^- < [Ms]^-$ as shown in figure 3.12. The IR spectra shown in the first column of figure 3.13 cover a large temperature range between 213 and 353 K. They are all obtained by subtracting the spectrum of the corresponding IL, deuterated at the OH position. This way, overlapping CH contributions are subtracted and the OH stretching region can be

adequately deconvoluted in all cases. The deconvolution at the lowest temperature of 213 K for all four ionic liquids is also presented in figure 3.13 as a second column. For all other temperatures, the deconvolution can be found in the **supporting information of publication IV**. The first interesting point to mention is the frequency of the c-a vibrational bands. It decreases from 3544 cm^{-1} for $[BF_4]^-$ over 3534 cm^{-1} for $[NTf_2]^-$ and 3438 cm^{-1} for $[Tf]^-$ down to 3313 cm^{-1} for $[Ms]^-$. A redshift of more than 200 cm^{-1} indicates the large difference in interaction strength between the observed anions.
Comparing the deconvoluted spectra, it has to be mentioned that only the spectrum of [HEMIm][Ms] can be perfectly described by one single voigt function, indicating that only one configuration of the cation is present in this ionic liquid. The line shape is ideal and symmetric. Due to the large interaction strength of the $[Ms]^-$ anion, the hydrogen bond is present between the anion and the cation. Cationic cluster formation is suppressed this way. For the three other ionic liquids more than one voigt profile is necessary to describe the experimentally obtained spectra. Thus, the OH group is included in more than one configuration realized by the presence of hydrogen bonded clusters between the $[HEMIm]^+$ cations. Due to the fact that the $[Tf]^-$ anion is still strongly interacting, the amount of cationic clusters is not large for this ionic liquid. Only for the weakly interacting $[NTf_2]^-$ and $[BF_4]^-$ anions the correlating ionic liquids show an appreciable amount of cationic clusters, indicated by high intensity redshifted contributions in the spectra, especially at lower temperatures.
To confirm this interpretation, an additional experiment, shown in the third column of figure 3.13, was done. Evaluating the intensity of the pure ILs [HEMIm][anion] (red) and those of their 10 mol% mixtures in [PMIm][anion] multiplied by a factor of ten (grey), it should be obvious which ionic liquids form cationic clusters and which not. All spectra presented in the third column of figure 3.13 are measured at 353 K, because the ionic liquid mixtures show phase transitions while cooling at different, but higher temperatures than 213 K. Due to the low OH density in the 10 mol% mixtures, only cation-anion pairs are present, similarly to the case for pure ionic liquids with strongly interacting anions. Therefore, for [HEMIm][Ms] both spectra (pure IL and 10 mol% mixture multiplied by a factor of ten) show nearly the same intensity, indicating the same amount of configurations, namely only cation-anion pairs. For all other ionic liquids, the intensity of the 10 mol% mixture, multiplied by a factor of ten, does not describe the experimental spectrum of the pure ionic liquids. Instead, there is a lot of redshifted intensity left stemming from the hydrogen-bonded clusters between the cations. This is a further proof that cationic cluster formation is only possible if the Coulombic interaction within the ion pair is lowered by weakly coordinating anions. These results are further used to show the effect

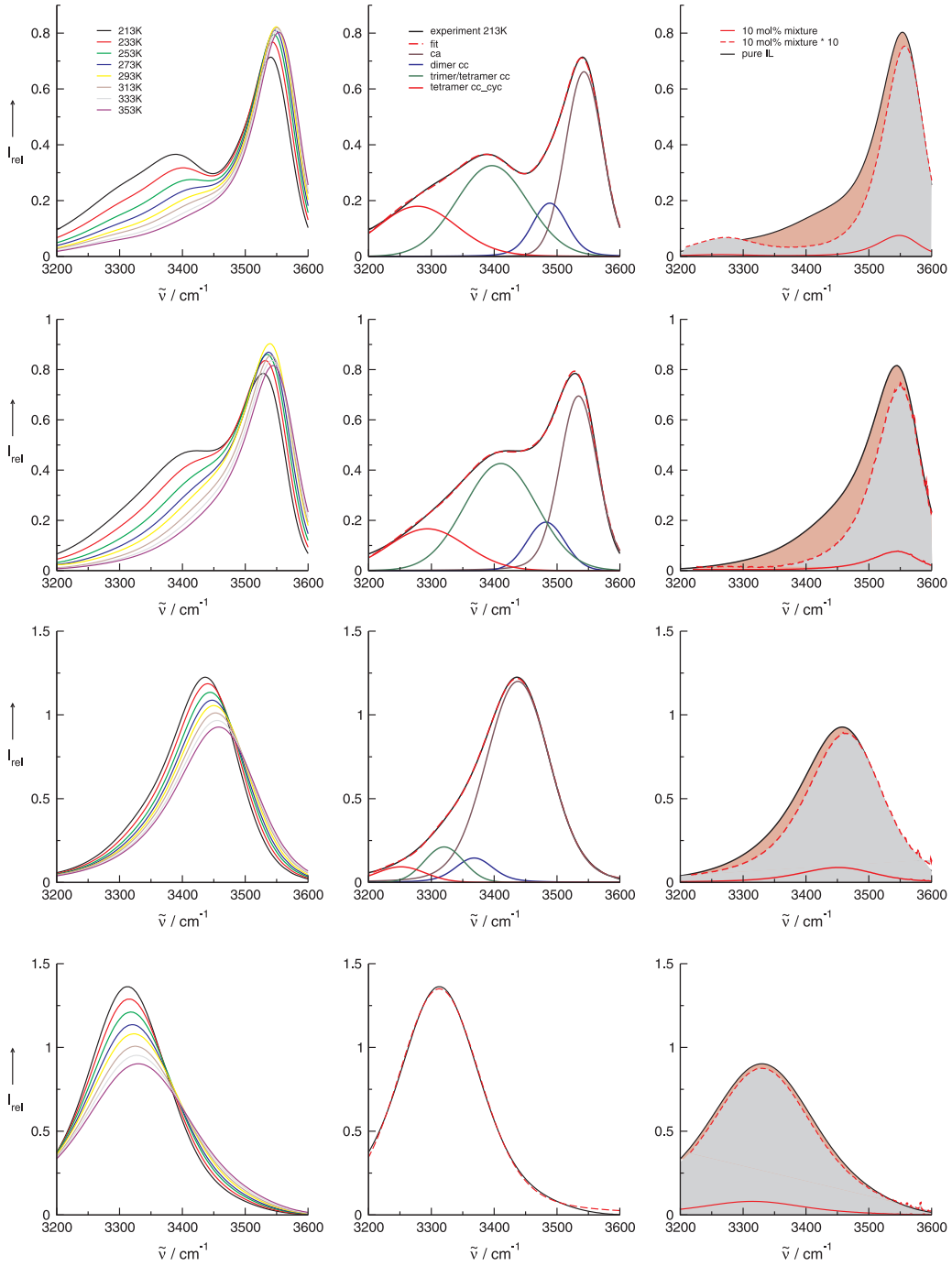

Figure 3.13: 1st column: MIR spectra in the OH-stretching region for a) b) c) and d)
2nd column: Deconvoluted MIR spectra at 213 K
3rd column: Comparison between MIR spectra of the pure ionic liquids and 10 mol% mixtures at 353 K.

of cationic cluster formation with NMR spectroscopy. For this purpose, the proton chemical shifts δ^1H have been measured versus TMS as a reference substance in a temperature range between 279 and 406 K. Due to the fact that this method is much slower than IR spectroscopy, it is not possible to find separated signals for different configuration of the OH group at the cation. Instead, only one average signal for all the hydroxyl protons is found. As known from the IR measurements, all ILs mainly consist of c-a ion pairs at high temperatures. Thus, the δ^1H values at 406 K, namely 2.84 ppm, 2.73 ppm, 3.52 ppm and 5.18 ppm for the four [HEMIm]-based ILs, reflect the different interaction strength of their anions in the order $[BF_4]^- \approx [NTf_2]^- < [Tf]^- < [Ms]^-$. For further evidence of the hydrogen bonded clusters between the cations at lower temperatures, it is necessary to use another suitable illustration of the data.
For that reason, the proton chemical shifts δ^1H of the hydroxyl protons in the pure ILs [HEMIm][anion] and their 10 mol% mixtures in [PMIm][anion] ILs have been measured as a function of temperature. In the first row of figure 3.14 the data is plotted on the left for [HEMIm][Ms] as an example of an ionic liquid without any cationic cluster formation and on the right for [HEMIm][BF_4] as an example of an ionic liquid with a lot of cationic cluster formation, especially at low temperatures. In general, it can be observed that firstly, the proton chemical shifts δ^1H increase while cooling and secondly, that the values for the OH group in the 10 mol% mixtures in [PMIm][anion] are slightly downfield-shifted compared to those in the pure ionic liquids. The hydrogen bond in the ion pairs is enhanced in the more hydrophobic environment of the [PMIm][anion] ILs, wherein the hydrophilic hydroxyl groups are missing.

Finally, cationic cluster formation should be indicated by different temperature behavior of the proton chemical shifts for the pure ILs and 10 mol% mixtures. But obviously the slope for the pure ionic liquid and the 10 mol% mixture is nearly the same for [HEMIm][Ms], including the strongly interacting methylsulfonate anion. This behavior reflects that in both cases all hydrogen bonds are just formed within the ion pair even at low temperatures. Clusters between the cations are not found in both cases. For better visualizing of the effects of anion and temperature, the chemical shift values for the pure ILs and their 10 mol% mixtures are overlaid at the highest temperature (see second column of figure 3.14). For the other ionic liquids, like [HEMIm][BF_4], the behavior is completely different. Now, the proton chemical shifts of the pure ILs are stronger downfield shifted than those of the 10 mol% mixtures which consist solely of c-a ion pairs over the whole temperature range. Thus, the stronger downfield shifts of the pure ILs indicate the formation of cationic clusters in accord with the IR results. Obviously, the equilibrium between the c-a and the c-c cluster species is shifted towards the cationic clusters at low temper-

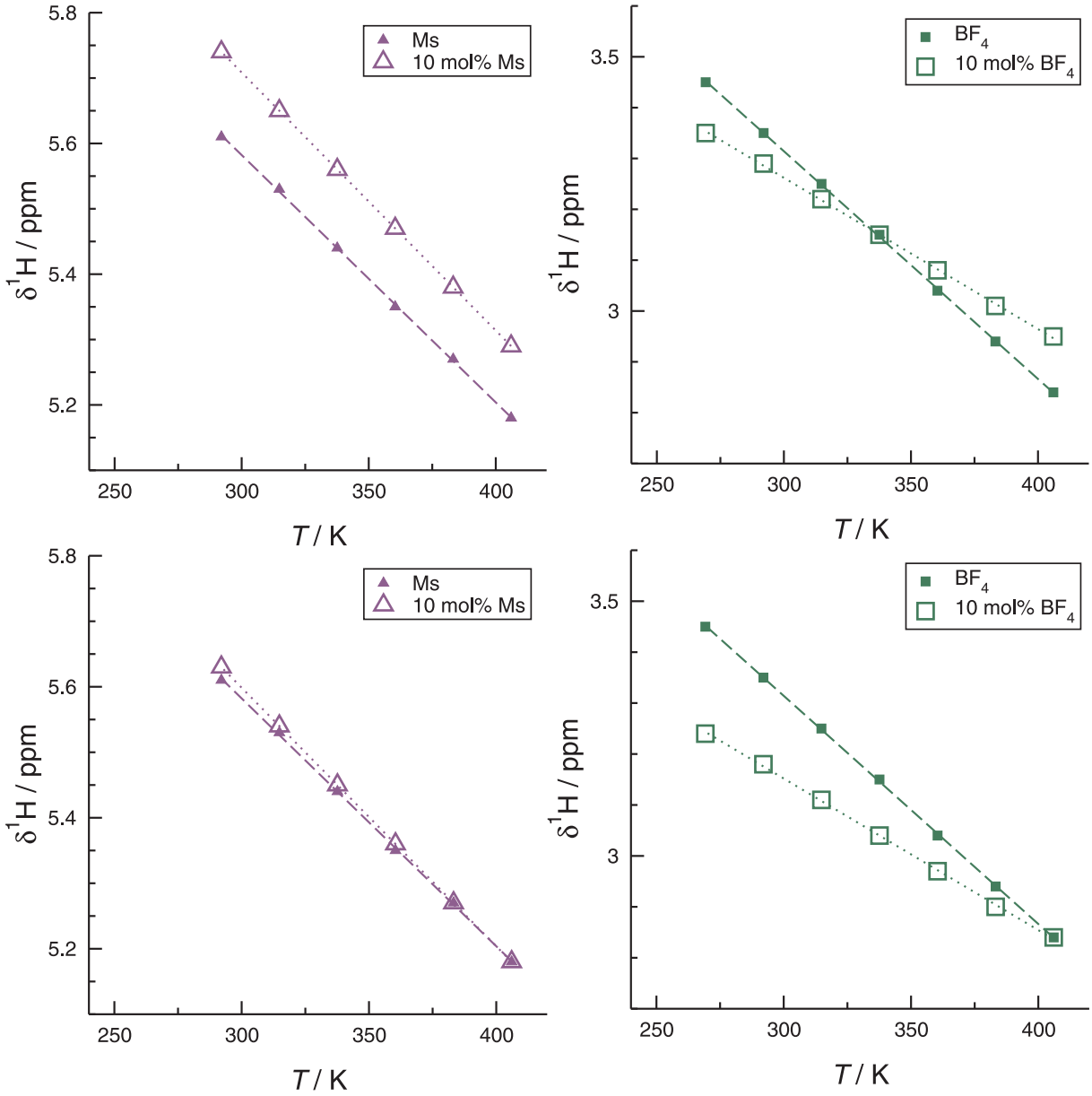

Figure 3.14: Measured proton chemical shifts $\delta^1 H_{OH}$ for [HEMIm][Ms] (left) and for [HEMIm][BF_4] (right)
1st row: measured values
2nd row: measured values overlaid at the highest temperature.

atures. The downfield shift caused by hydrogen bonding between the hydroxyl groups of the cations has been shown already in figure 3.9 for DFT-calculated chemical shifts of these cluster species. In spite of the strong repulsive forces between the like-charged ions, these strong and cooperative hydrogen bonds lead to significant deshielding of the hydroxyl protons as it is known for molecular liquids like water or alcohols. [125, 126]

3.4 Controlling kinetic and thermodynamic stability

Short introduction and motivation

While all chapters so far presented results about experimental studies of the liquid phase, this chapter is a description of the gas phase, solely based on quantum chemical calculations. The purpose of these studies is to answer the question whether it is also possible to observe differently charged cationic clusters in the gas phase experimentally, e.g., by methods like cryogenic ion vibrational predissociation spectroscopy (CIVP). [127] The Johnson group could already show cationic clusters of $[EMIm]_2[BF_4]^+$ with this method. [128, 129] In **publication V** the ionic liquid $[Ch][NTf_2]$ and the neutral equivalent to the cation, 3-3-dimethyl-1-butanol (DM1B), are chosen as model substances. B3LYP/6-31+G* calculations have been performed with the Gaussian09 program and analyzed with the NBO 6.0 program, [117, 118, 130] finally leading to strategies how to convert the clusters from the kinetically into the thermodynamically stable regime. This is important, because based on the very low temperatures during cryogenic measurements, mainly thermodynamically stable configurations are formed and detectable with these methods.

Comparison between molecular and cationic clusters

The cholinium cation and the molecular liquid DM1B are very similar in structure. The alcohol only differs from the cation by replacing the nitrogen with a carbon atom. For both, molecular and ionic liquids, cluster formation between either the cations (**publication I**) or the molecules is known. To compare the stability and the possible size of these clusters B3LYP-D3/6-31+G* calculations of different linear and cyclic ionic or neutral clusters have been performed. In figure 3.15 the binding energy per species for clusters of size n is presented for both cases.
As expected, the values for DM1B are negative, representing thermodynamic stability for all calculated configurations. The interaction strength is typically enhanced with increasing cluster size as it is known for molecular liquids. [104–108] Compared to the alcohol

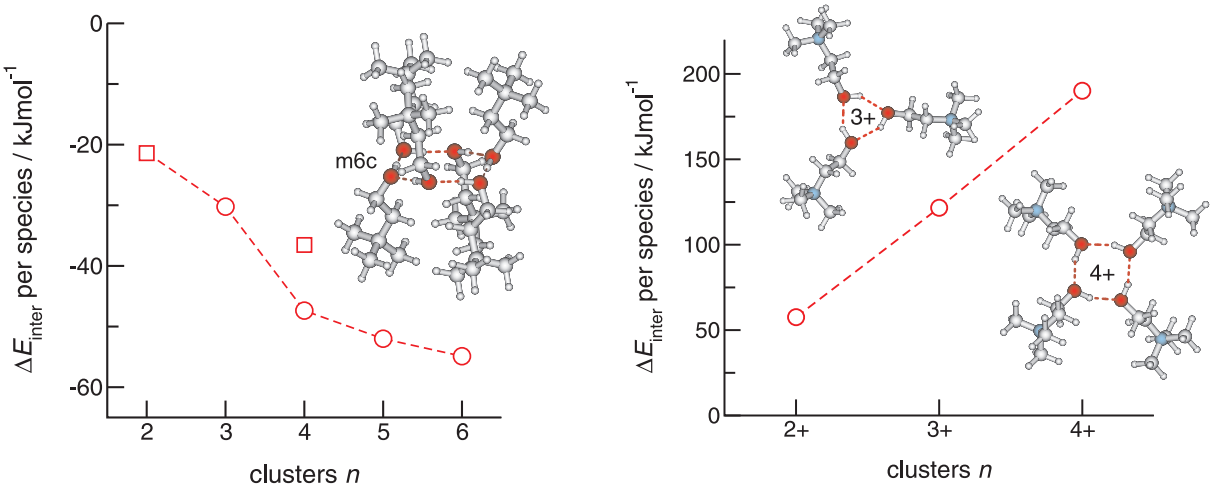

Figure 3.15: B3LYP-D3/6-31+G* calculated binding energies ΔE_{inter} per species for different sized clusters of DM1B (left) and $[Ch]^{n+}$ (right).

dimer, the interaction strength per molecule in the cyclic tetramer, pentamer and hexamer is even more than doubled. This behavior results from strong cooperative effects as already discussed in the previous chapters.

For the purely cationic clusters shown in figure 3.15 on the right the situation is a little bit different. It is only possible to optimize structures of dimers as well as cyclic trimers and tetramers, respectively. Linear trimers and tetramers as well as larger clusters like pentamers or hexamers are not metastable anymore. They dissociate during the geometry optimization procedure. The other configurations are kinetically, but not thermodynamically stable, indicated by positive values for the energies per species together with positive values for calculated IR frequencies. They are represented by a clear local minimum of about 5-7 kJ mol^{-1} on the potential energy curve as it is shown in figure 1 of **publication V**. The increasing energy per species with increasing cationic cluster size shown in figure 3.15 additionally indicates the stronger electrostatic repulsion that has to be compensated by attractive hydrogen bonding. So far, in contrast to molecular clusters, these purely cationic clusters probably will not be available experimentally.

Methods to stabilize cationic clusters

To be able to observe cationic clusters experimentally in the gas phase, it seems to be necessary to bring them from the kinetically stable to the thermodynamically stable regime. Therefore, two strategies have been developped and supported by DFT-D3 calculations.

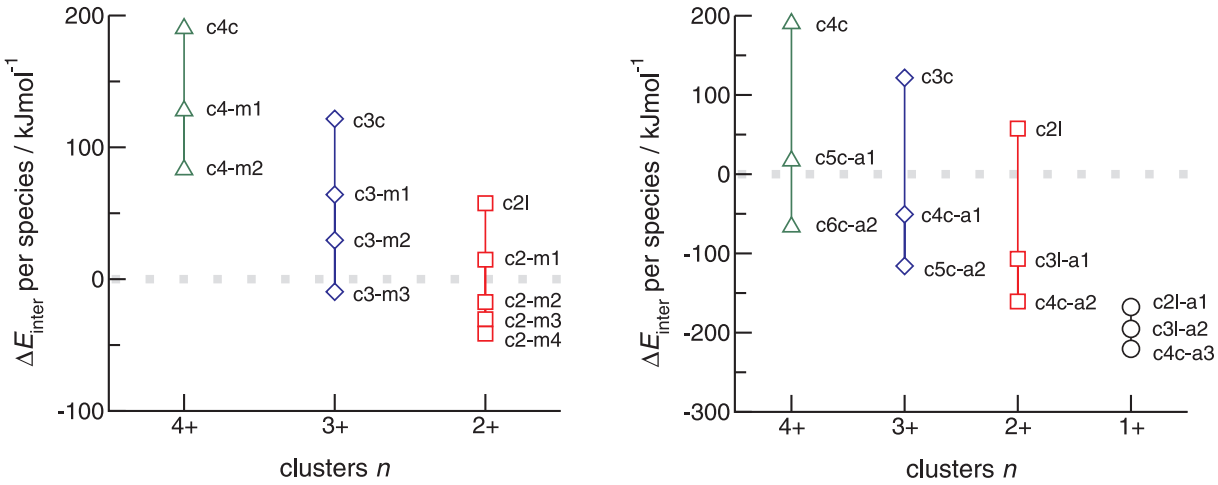

Figure 3.16: B3LYP-D3/6-31+G* calculated binding energies ΔE_{inter} per species for pure cationic clusters and those added by molecules (left) as well as for pure cationic clusters and those added by counter ions (right).

The first one is adding systematically neutral molecules to the multiple positively charged clusters. This way, the value of the charge remains stable while the repulsive Coulombic forces are weakened. A second possibility to further stabilize the cationic clusters is adding anions as part of additional ion pairs, while remaining the values of the positive charge, respectively. Both strategies have been applied to the linear dimer, cyclic trimer and cyclic tetramer as a starting point. The calculated binding energies per species are shown in figure 3.16 for the addition of molecules on the left and for the addition of counterions on the right. By adding neutral DM1B molecules, the linear dimer (c2l) can be stabilized. However, thermodynamic stability can be only achieved if a second molecule is added. This way, a cyclic tetramer (c2-m2) is formed. By adding even more alcohol molecules, the two times positively charged clusters can be further stabilized, resulting in cyclic pentamers (c2-m3) or hexamers (c2-m4). With this procedure the system is changed smoothly from the ionic into the molecular direction by distributing the charge step by step over larger clusters. To overcome the stronger repulsive Coulomb forces in the higher charged clusters, obviously more molecules are necessary. In the case of the cyclic trimer (c3c), three DM1B molecules are necessary to achieve thermodynamic stability within a cyclic hexamer (3c-3m). In both cases the cationic clusters become thermodynamically stable if every cation is neighbored by a DM1B molecule within a cyclic configuration. That is also the reason why it is not possible to bring the fourfold positively charged tetramer (4c4) into the thermodynamically stable regime. By adding one or two molecules, only further kinetic stabililty is achieved. But larger ring structures, such as heptamers or octamers,

exceed the size of the enthalpically and entropically favorable hexamer as known from studies of alcohol clusters.
At that point the second strategy of adding $[NTf_2]^-$ counterions instead of molecules could be applied. The single positively charged clusters c2l-a1, c3l-a2 and c4c-a3 are thermodynamically stable throughout. Thus, these clusters should be observable in the experiment as Johnson et al. have shown for another ionic liquid. [128, 129] Also, for the c2l and the c3c clusters only one additional anion is needed to create a thermodynamically stable configuration, while for the c4c cluster it is necessary to add two counterions. The effect on the stability of the cationic clusters by systematically adding anions is obviously larger than that of adding neutral molecules. This is mainly based on the large value of 300-400 kJ mol^{-1} that each ion pair contributes to the binding energy, which is well known from calculations of smaller aggregates of ionic liquids. [34, 40, 41, 84, 131, 132]

To summarize, it was shown that the addition of 3-3-dimethyl-1-butanol molecules as well as the addition of $[NTf_2]^-$ counterions to purely cationic cholinium clusters results in enhanced kinetic stability and in some cases even in thermodynamic stability. Especially the thermodynamically stable clusters should be observable in sophisticated gas phase experiments such as CIVP spectroscopy.

4 Summary and Outlook

Within this PhD study, the new counterintuitive phenomenon of like charge attraction between cations in ionic liquids was described in detail for the first time. Due to the fact that ionic liquids solely consist of charged particles, the known and expected situation would be to find ion pairs of oppositely charged ions in the bulk phase. But indeed, depending on the molecular structure of the ionic liquid, cationic clusters of different sizes up to cyclic tetramers could be found. For this, spectroscopic as well as theoretical evidence have been presented.
It could be shown that the repulsive Coulombic interaction between the like-charged cations can be attenuated by cooperative hydrogen bonding comparable to that in molecular solvents like water or alcohols. Therefore, hydroxyl groups as H-bond forming functional groups are introduced to the cation. To increase the distance between the positive charge center and the OH group, an additional ethyl group was introduced as a spacer. And finally, it could be shown that the formation of cationic clusters in ionic liquids requires a lowering of the attractive Coulombic interaction within the ion pair by choosing weakly coordinating anions.
First of all, it could be shown that especially IR spectroscopy in the mid-infrared region is useful to distinguish between different kinds of hydrogen-bonded species. The cationic clusters (c-c) show additional redshifted signals compared to the hydrogen bond within an ion pair of cation and anion (c-a). These contributions could be clearly assigned to OH vibrational modes by OD deuteration experiments. Both species exist in equilibrium while the c-c cationic clusters are favored at lower temperatures. Experimentally, the strong and cooperative OH$\cdots$OH hydrogen bonds within these clusters result in redshifts of the OH vibrational frequencies compared to that of an OH group interacting with the anion as well as in downfield shifts of the proton chemical shifts. This indicates stronger hydrogen bonds within the cationic clusters compared to those within the ion pairs. With the support of density functional theory calculations, this fact is also reflected in decreasing intramolecular R(OH) bond lengths as well as increasing intermolecular R(O$\cdots$H) and R(O$\cdots$O) bond distances with increasing cluster size. The cooperative effect could further be confirmed by the assignment of NBO analysis. Increasing charge transfer as

well as increasing second order stabilization energies can be correlated with the spectroscopic observables. To summarize, this is the first complex study that combines detailed experimental and theoretical results to explain the cluster formation between ions of like charge in ionic liquids based on hydrogen bonding.
Nevertheless, for a full description of this counterintuitive phenomenon a lot of open questions remain. One of the most important points is the dependence of the cationic cluster formation on the molecular structure of the cation, focusing on aspects like charge localisation or delocalisations as well as shielding effects, respectively. Additionally, it is already known, but not sophisticatedly studied, that the equilibrium between the c-a and the c-c clusters is also signifiantly dependent on the chain length of the hydroxyalkyl chain. Comparing cations with hydroxyethyl or hydroxypropyl groups, cationic cluster formation should be even favored in the second case. Another interesting issue, based on the molecular structure of the ionic liquids, is the question whether the cationic cluster formation could influence macroscopic properties, such as melting points, viscosities or even phase transition behavior. Those aspects are especially important with regard to the application of ionic liquids as solvent media.
All results that have been discussed in this PhD thesis are based on the attractive interaction between positively charged cations. For the future it could be very interesting to think about ionic liquids with the potential of attractive hydrogen bonding between the negatively charged anions. This task probably includes additional synthesis work because, instead of the common anions, functionalized ones, e.g., oxalate are required.
Finally, it can be said that this interesting topic of like charge attraction in ionic liquids is not described exhaustively so far. Thus, the results of this PhD study could be the fundament for further investigations.

5 Publications

		Contribution
I	A. Knorr, K. Fumino, A.-M. Bonsa, R. Ludwig, 'Spectroscopic evidence for 'jumping and pecking' of cholinium and H-bond enhanced cation-cation interaction in ionic liquids', *Phys. Chem. Chem. Phys.*, **2015**, 17, 30978-30982.	Communication **50%**
II	A. Knorr, R. Ludwig, 'Cation-cation clusters in ionic liquids: Cooperative hydrogen bonsing overcomes like-charge repulsion', *Sci. Rep.*, **2015**, 5, 17505.	Communication **70%**
III	A. Knorr, P. Stange, F. Weinhold, R. Ludwig, 'Spectroscopic evidence for clusters of like-chraged ions in ionic liquids stabilized by cooperative hydrogen bonding', *Chem. Phys. Chem.*, **2016**, 17, 458-462.	Communication **60%**
IV	A. Strate, T. Niemann, D. Michalik, R. Ludwig, 'When like charges attract in ionic liquids: Controlling the formation of cationic clusters by the interaction strength of the counterions', *Angew. Chem. Int. Ed.*, **2017**, 56, 496-500.	Communication **65%**
V	A. Strate, T. Niemann, R. Ludwig, 'Controlling the kinetic and thermodynamic stability of cationic clusters by the addition of molecules or counterions', *Phys. Chem. Chem. Phys.*, **2017**.	Full Paper **35%**

5.1 Publication I

Communication: *Phys. Chem. Chem. Phys.*, **2015**, 17, 30978-30982.

Spectroscopic evidence for 'jumping and pecking' of cholinium and H-bond enhanced cation-cation interaction in ionic liquids

Anne Knorr (50%), Koichi Fumino (10%), Anne-Marie Bonsa (10%) and Ralf Ludwig (30%)

Received 12th June 2015, Accepted 6th August 2015

DOI: 10.1039/c5cp03412d

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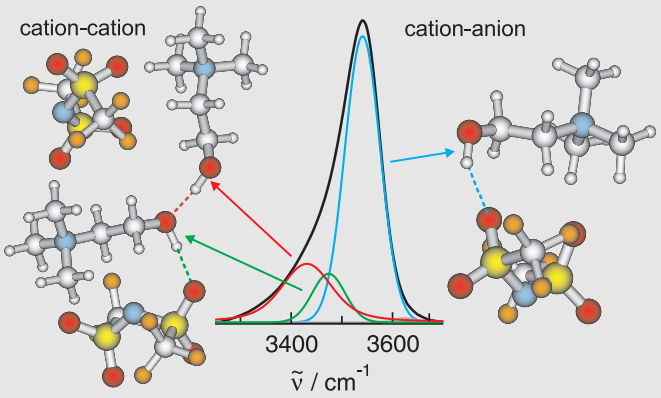
The first time direct spectroscopic evidence for attractive interaction between ions of like charge could be found in an ionic liquid. The repulsive Coulombic interaction between the cations is overcome by cooperative hydrogen bonding.



Contribution to this work (50%)

I had the main ideas for this paper and wrote a first draft. I've done all the Mid-IR and Far-IR measurements for the ionic liquid as well as the deconvolution of the spectra. Experimentally this work was supported by Koichi Fumino with a spectrum of ethanol and by Anne-Marie Bonsa with viscosity measurements. Professor Ralf Ludwig contributed to the work with some DFT-calculations and received the manuscript for final corrections.

5.2 Publication II

Communication: *Sci. Rep.*, **2015**, 5, 17505.

Cation-cation clusters in ionic liquids: Cooperative hydrogen bonsing overcomes like-charge repulsion

Anne Knorr (70%) and Ralf Ludwig (30%)

Received 1st October 2015, Accepted 28th October 2015

DOI: 10.1038/srep17505

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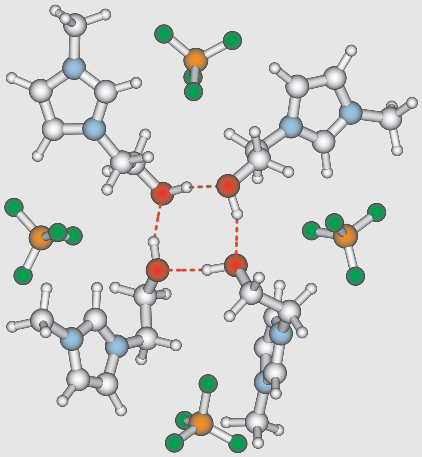
In [HEMIm][BF_4] new IR contributions in the OH-stretching region appear at low temperatures. They indicate the formation of differently sized linear and cyclic cationic clusters. The experimental findings and DFT calculations strongly support the concept of anti-electrostatic hydrogen bonding (AEHBs).



Contribution to this work (70%)

I had the main idea of influencing the amount of cationic clusters by changing the molecular structure of the ionic liquid compared to publication I. I performed all the experiments for this publication as well as writing a draft for the manuscript. Professor Ralf Ludwig supported the work with DFT calculations and got the manuscript for final corrections.

5.3 Publication III

Communication: *Chem. Phys. Chem.*, **2016**, 17, 458-462.

Spectroscopic evidence for clusters of like-charged ions in ionic liquids stabilized by cooperative hydrogen bonding

Anne Knorr (60%), Peter Stange (10%), Frank Weinhold (10%) and Ralf Ludwig (20%)

Received 8th December 2015, Accepted 16th December 2015

DOI: 10.1002/cphc.201501134

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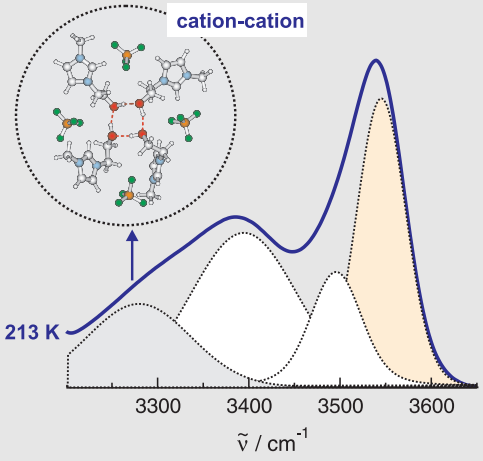
The cationic clusters in the ionic liquid [HEMIm][BF_4] are kinetically stabilized by cooperative hydrogen bonding at low temperature. The intra- and intermolecular bond distances show the same behavior compared to molecular clusters of water or alcohols. While diluting the OH density the cluster contributions disappears below a concentration of 10 mol%.



Contribution to this work (60%)

I have written the manuscript and performed all the spectroscopical investigations for ionic liquids as well as the deconvolution and interpretation. Experimentally this work was supported by Peter Stange with an spectrum of propanol. Professor Frank Weinhold contributed with NBO analysis while Professor Ralf Ludwig did further DFT-calculations. Both received the manuscript for final corrections.

5.4 Publication IV

Communication: *Angew. Chem. Int. Ed.*, **2017**, 56, 496-500.

When like charges attract in ionic liquids: Controlling the formation of cationic clusters by the interaction strength of the counterions

Anne Strate (65%), Thomas Niemann (20%), Dirk Michalik (5%) and Ralf Ludwig (10%)

Received 6th October 2016, Published 19th December 2016

DOI: 10.1002/anie.201609799

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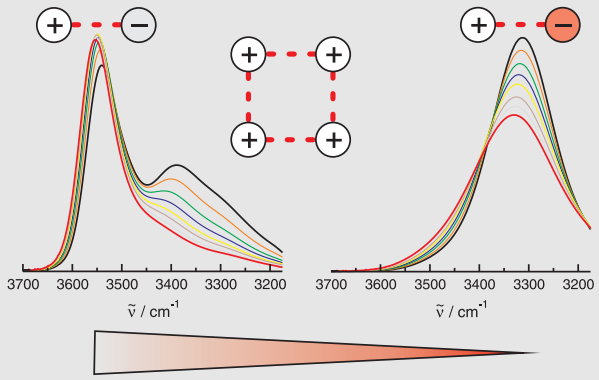
By choosing weakly coordinating anions, the attractive Coulombic interaction can be lowered leading to the formation of cationic clusters. Based on IR and NMR signatures a simple but effective spectroscopic scale for the possibility of this cluster formation is presented.



Contribution to this work (65%)

I had the main ideas for controlling the amount of cationic cluster formation by choosing differently strong interacting anions. I have done most of the Mid-IR measurements as well as the deconvolution of the spectra and I wrote a first draft. One ionic liquid was measured by Thomas Niemann. Dirk Michalik contributed to the work with NMR measurements and Professor Ralf Ludwig received the manuscript for final corrections.

5.5 Publication V

Full paper: *Phys. Chem. Chem. Phys.*, **2017**.

Controlling the kinetic and thermodynamic stability of cationic clusters by the addition of molecules or counterions

Anne Strate (35%), Thomas Niemann (30%) and Ralf Ludwig (35%)

Received 6th April 2017, Accepted 21th June 2017

DOI: 10.1039/c7cp02227a

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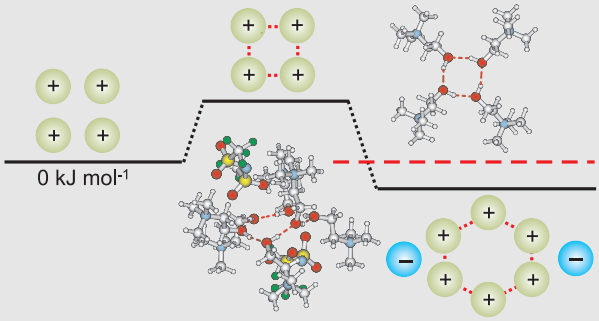
The charge, the size and the structural motifs of cationic clusters in the gas phase are investigated. Compared to the neutral ionic liquids, the positive charges are not always fully balanced by anions in the gas phase.



Contribution to this work (35%)

To this publication the authors contributed nearly equally. All three authors did some of the DFT calculations. Professor Ralf Ludwig wrote the manuscript, while Thomas Niemann and I got it for final corrections.

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Doktorandinnen/Doktoranden-Erklärung gemäß § 4 Absatz 1 Buchstaben g und h der Promotionsordnung der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock

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Ich habe eine Dissertation zum Thema

Spectroscopic Evidence for Clusters of like-charged Ions in Ionic Liquids

an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock angefertigt. Dabei wurde ich von Frau/Herrn

Prof. Dr. Ralf Ludwig

betreut.

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